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THE SOLUBILITY RELATIONS OF THE RARE EARTH OXALATES

A Thesis
Submitted to the Faculty of the Graduate School
of the
University of Minnesota
in Partial Fulfillment of the Requirements
for the Degree of
Doctor of Philosophy

by

Landon Arndale Sarver

July 1924

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ACKNOWLEDGEMENT

THE SOLUBILITY RELATIONS OF THE RARE EARTH OXALATES

INTRODUCTORY

The present state of our knowledge of the rare earth group is far from satisfactory, and what is needed above everything else is exact information on the chemistry of these elements. The foundation of all exactness in the study of a chemical group is absolute mastery of the reactions entering into the analytical processes of the elements of the group; and the one reaction which is most characteristic of the rare earth elements is the precipitability of their oxalates in faintly acid solution.

In the course of a recent investigation it became necessary to determine the strengths of a large number of solutions of rare earth elements, and in the case of some of these it was found impossible to obtain concordant results by precipitation as oxalate. Some of the less basic had to be precipitated as hydroxide. It was thought that the concentration of mineral acid and excess oxalic acid might have more

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RARE EARTH OXALATES

INTRODUCTION

effect on the solubility of the oxalates than had been generally supposed.

A survey of the existing data showed that the literature on the subject was scattered, fragmentary, and somewhat contradictory. Therefore, it seemed desirable to make a critical study of all existing information on the solubilities of the rare earth oxalates, and to supplement and recheck these values by work on very highly purified material, so that the completed research should constitute a fairly complete study of the subject.

Frequent reference to the insolubility of the oxalates in a qualitative way is found in the literature[1], but the first approach to anything specific is a statement by Cleve and Hoeglund[2] that one part of yttrium oxalate dissolves in 7163 parts of water, and 494.6 parts of 3.705 % hydrochloric acid; that it is easily soluble in a concentrated solution of potassium oxalate; but that only a trace is dissolved by ammonium oxalate. The temperatures are not given, however.

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1. Vauquelin, Ann. de chim., 50, 140 (1804); Berzelius and Hisinger, Ibid., 50, 245 (1304); Mosander, Ibid., III, 11, 464 (1844); Marignac, Annalen, 88, 232 (1853).

2. Cleve and Hoeglund, Bull. Soc. Chim., 18, 239 (1872).

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Frequent reference to the insolubility of the oxalates in a qualitative way is found in the literature[1], but the first approach to anything specific is a statement by Cleve and Hoagland[2] that one part of yttrium oxalate dissolves in 7185 parts of water, and 191.6 parts of 4.05 % hydrochloric acid; that it is easily soluble in a concentrated solution of potassium oxalate; but that only a trace is dissolved by ammonium oxalate. The temperatures are not given, however.

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1. Vauquelin, Ann. de chim., 50, 140 (1804); Berzelius and Nielsgen; Ibid., 90, 240 (1304); Woodcock; Ibid., III, 17, 104 (1814); Berlingo, Ann.Phen, 88, 252 (1852).

2. Cleve and Hoagland, Bull. Soc. Chim., 18, 239 (1872).

The first really reliable contribution was by Brauner[1], who determined the solubilities of lanthanum, cerium, praseodymium, neodymium, and yttrium oxalates at 20° C. in ammonium oxalate (1 gram in 38 grams of water), and in normal sulfuric acid. He was followed by Scheele[2], who determined the solubilities of praseodymium and lanthanum oxalates in two concentrations of nitric acid. Benedicks[3] gives values for gadolinium oxalate in ammonium oxalate (1 gram in 38 grams of water), and in normal sulfuric acid. Cleve[4] gives similar data for ytterbium.

After a lapse of several years a number of investigators[5] published papers on the occlusion of alkali oxalates and ammonium oxalate by rare earth oxalates, but these papers deal with the molecular compositions of liquid and solid phases rather than with solubilities.

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1. Brauner, J. Chem. Soc., 73, 951 (1898).

2. Scheele, Ber., 32, 409 (1899).

3. Benedicks, Zeitschr. anorg. Chem., 22, 393 (1900).

4. Cleve, Zeitschr. anorg. Chem., 32, 129 (1902).

5. Baxter and Griffin, J. Am. Chem. Soc., 28, 1684 (1907);
   Baxter and Daudt, Ibid., 30, 563 (1909);
   Pratt and James, Ibid., 33, 488 (1911).

The first really reliable contribution was by Durrer[1], who determined the solubilities of lanthanum, cerium, praseodymium, neodymium, and yttrium oxalates at 20° C. In ammonium oxalate (1 gram in 75 grams of water), and in neutral nitric acid. He was followed by Robards[2], who determined the solubilities of praseodymium and lanthanum oxalates in two concentrations of nitric acid. Jamalova[3] gives values for lanthanum oxalate in ammonium oxalate (2 grams in 50 grams of water), and in neutral nitric acid. Clarke[4] gives similar data for yttrium.

After a large of several years a number of investigators[5] published papers on the separation of alkali oxalates and ammonium oxalate by recrystallization, but those papers

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1. Durrer, J. Chem. Soc., 125, 2211 (1924).
2. Robards, Ber., 32, 409 (1899).
3. Jamalova, Chem. Zentr., 1924 I, 2844 (1900).
4. Clarke, Zeitschr. anorg. Chem., 285, 129 (1902).
5. Baxter and Griffin, J. Am. Chem. Soc., 28, 1284 (1906).
   Baxter and Davis, ibid., 30, 856 (1908).
   Prandtl and Jaeger, ibid., 33, 433 (1911).

By far the greatest contributions to the subject have been made by Hauser, Wirth, Meyer, and co-workers[1], who give information on the solibilities of lanthanum, cerium, and samarium oxalates in sulfuric and oxalic acids, along with a few determinations for cerium and neodymium oxalates in hydrochloric acid solutions. They also give some transition concentrations for lanthanum oxalate (to lanthanum sulfate) in sulfuric acid solutions at 25° C. Rimbach and Schubert[2], and Hauser and Herzfeld[3] determined the solubilities of lanthanum, cerium, praseodymium, neodymium, samarium, yttrium, and ytterbium oxalates in water at 25° C., using the electrical conductivity method as well as gravimetric and volumetric methods, but good agreement between the different methods was not obtained. Finally, in 1917, Grant and James[4] determined the solubilities of lanthanum, neodymium, gadolinium, dysprosium, yttrium, thulium, and ytterbium oxalates in 20 % methyl-amine oxalate, ethyl-amine oxalate, and tri-ethyl-amine oxalate.

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1. Hauser and Wirth, Zeitschr. anal. Chem., 47, 389 (1908);
   Hauser and Wirth, Zeitschr. prakt. Chem., 79, 358 (1909);
   Wirth, Zeitschr. anorg. Chem., 58, 213 (1908);
   Wirth, Ibid., 76, 174 (1912);
   Meyer and Hauser, Book: "Seltenen Erden und Erdsauren", 59;
   Hauser and Herzfeld, Generrich, Meyer and Wassuchnow, Op.cit.
2. Rimbach and Schubert, Zeitschr. phys. Chem., 67, 183 (1909).
3. Hauser and Herzfeld, Loc. cit.
4. Grant and James, J. Am. Chem. Soc., 39, 933 (1917).

Altho existing information for the whole rare earth series is meager, it has been impossible up to the present time to obtain all the materials in a sufficiently high state of purity; and in this dissertation the elements of the cerium group, and one element, gadolinium, of the intermediate terbium group have been investigated. It is hoped that the study which has been made with these elements, and the improvement of experimental methods of procedure, which presented great obstacles to reliable determinations, will greatly facilitate any subsequent work.

EXPERIMENTAL

Lanthanum Oxalate.- The purest lanthanum ammonium nitrate was procured thru the courtesy of Dr. H. S. Miner, of the Welsbach Company, Gloucester, New Jersey. Examination of a saturated solution thru a layer 10 centimeters thick by means of a high grade direct vision spectroscope showed no trace of absorption lines. The arc spectrum was then photographed with a quartz spectrograph (Fig. 1), and this also showed the material to be entirely free from other rare earths. Nevertheless, to be on the safe side, the whole batch was treated with ammonia and hydrogen peroxide in such a manner that a small amount of lanthanum was precipitated, along with which any cerium present would be completely

removed. The ammonia-hydrogen peroxide test showed no trace of cerium, and the purity of the material was assured beyond reasonable doubt. The lanthanum was then precipitated three times as oxalate from very dilute sulfuric acid solution, very thoroly washed, and finally dried at 105° C.

Cerous Oxalate.- A sample of cerous sulfate was kindly supplied by Professor Charles James, of the University of New Hampshire. This was said to be free from other rare earths, but to contain small amounts of iron and calcium. It was dehydrated to render it soluble, dissolved in ice water, acidified with hydrochloric acid, and precipitated in the cold with an excess of oxalic acid. After air-drying, this was fumed with sulfuric acid, redissolved in ice water, and precipitated as sulfate by mixing with an equal volume of 95 % ethyl alcohol. The product was again dehydrated, redissolved, and precipitated by concentrating the solution. This was dehydrated, dissolved, and precipitated as oxalate; converted to sulfate by fuming with sulfuric acid, dissolved, and precipitated as sulfate by mixing with alcohol; dehydrated and dissolved again, and finally precipitated three times as oxalate. This product was dried at 105° C., and examined for other rare earths by arc and absorption spectra. These tests showed no trace of impurities.

Praseodymium Oxalate.- The praseodymium material was obtained in the form of ten fractions which had come originally from Travancore monazite, and had been fractionally crystallized several hundred times as the double ammonium nitrate. The fractionation as double ammonium nitrate was continued fifty times more; and then the two purest fractions were precipitated separately twice as oxalates, and dried at 105° C. The absorption and arc spectra showed no impurities in either fraction, so the two were combined.

Neodymium Oxalate.- A large sample of neodymium ammonium oxalate was obtained from the Welsbach Company, and found to be quite impure. While no samarium absorption lines were visible, those of praseodymium showed very plainly. The material was converted to the double neodymium manganese nitrate, and fractionation begun in nitric acid of specific gravity 1.300. After a few crystallizations, considerable praseodymium and lanthanum had collected at the less soluble end, and these fractions were removed from the system. All the fractions were occasionally precipitated as oxalate and reconverted to the double neodymium manganese nitrate, in order to eliminate impurities which had accumulated in the fractions in amounts sufficient to interfere with the crystallization. After fifty crystallizations as the double salt, the two purest fractions were converted to

the simple nitrates, and crystallized thirty times more. The order of solubility was thus reversed. At the end of this fractionation, no praseodymium lines could be detected in the absorption spectra of the three purest fractions. These were then precipitated three times as oxalate, and then dried at 105° C. Photographs of the arc spectra were then made, and these showed the material to be of the highest degree of purity.

Samarium Oxalate.- The samarium sample was prepared from the material used by Stewart and James[1] for the determination of the atomic weight of samarium. It was converted from the sulfate to the oxalate in the conventional way, and dried at 105° C. The arc and absorption spectra were then examined, and no impurities found.

Gadolinium Oxalate.- The gadolinium material was also pure, having been used by Brinton and James[2] in the study of the hydrolysis of the carbonate. It was entirely free from absorption lines in the visible region, and the arc spectrum also showed it to be very pure.

The photographs of the arc spectra of all these elements are shown in Figure 1, compared with the lines of the carbon electrodes, and these give visible proof of the purity of all materials.

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1. Stewart and James, J. Am. Chem. Soc., 39, 2605 (1917).
2. Brinton and James, Ibid., 43, 1446 (1921).

Recovery of materials.- The small amounts of the rare earth oxalates available made the work very tedious, due to the fact that the entire amount of material was frequently required for a single determination, and had to be recovered before another could be made. The excess solid and solutions were carefully rinsed into large beakers; the ignited oxide residues were dissolved in hydrochloric acid, and added to the main portions;the whole was then nearly neutralized with ammonia, whereby most of the oxalate was precipitated, and an excess of oxalic acid then added. The mixtures were allowed to stand an hour or two so that any rare earth chloride, sulfate, or nitrate in the solid phase would be converted to oxalate. The precipitates were then filtered off, thoroly washed, and dried at 105° C.

In this investigation, several experimental difficulties have been overcome, and solubilities measured for the six elements: lanthanum, cerium, praseodymium, neodymium, samarium, and gadolinium in the following solvents:

1. Water (both by gravimetric and by conductivity methods);
2. Hydrochloric acid of varying concentrations;
3. Nitric acid of varying concentrations;
4. Sulfuric acid of varying concentrations;

5. Tenth-normal oxalic acid with varying concentrations of hydrochloric acid;

6. Tenth-normal oxalic acid with varying concentrations of nitric acid;

7. Half-normal oxalic acid with varying concentrations of hydrochloric acid;

8. Half-normal oxalic acid with varying concentrations of nitric acid;

9. Varying concentrations of hydrochloric acid saturated with oxalic acid;

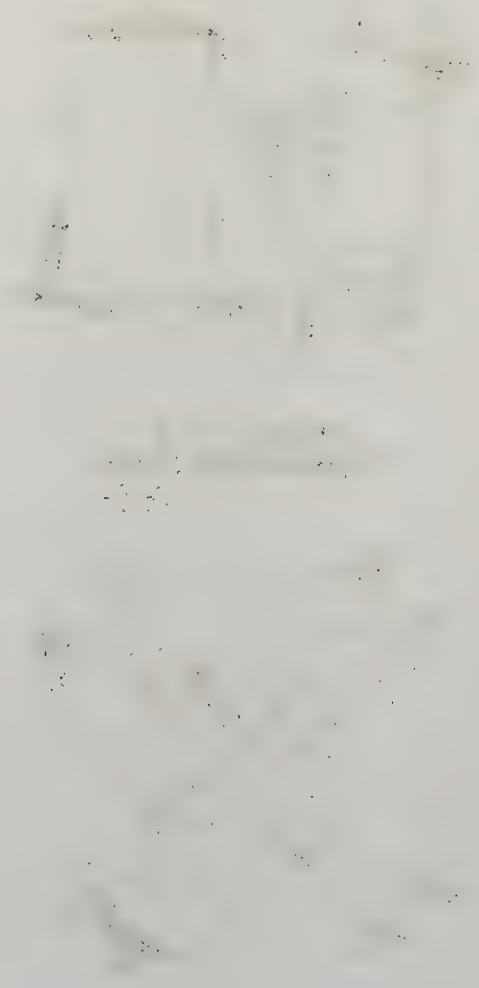
10. Varying concentrations of nitric acid saturated with oxalic acid.

Thermostat. There was not to be found on the market a thermostat of sufficient size and suitable construction for the purposes of this research, so it was necessary to design and build one to meet our particular needs. It was made of alberene stone one inch thick, and the outside dimensions of the whole tank are fifty-three (53) by thirty-three (33) by thirty-six (36) inches (Figure 2). A heavy steel shaft with worm gear, carrying specially constructed bronze frames (Figure 3) to hold the bottles, was hung horizontally on cast iron bearings which were supported by well-painted iron cradles at each end inside the tank. A vertical driving shaft,

in mesh with the worm gear, and reaching several inches above the top of one end of the tank, is driven by a quarter horsepower continuous-duty electric motor mounted on steel brackets on top and outside of the tank.

Figure 2
Thermostat Tank

Figure 3
Bottle Frame Detail



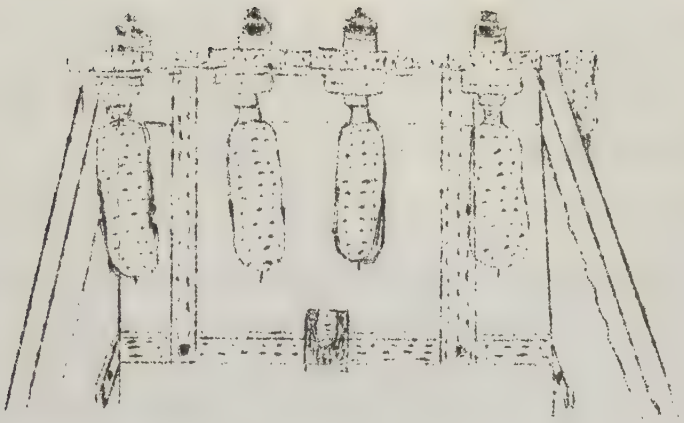


Figure 4
Heating Bulbs, Hanger Cradle, and Bearing

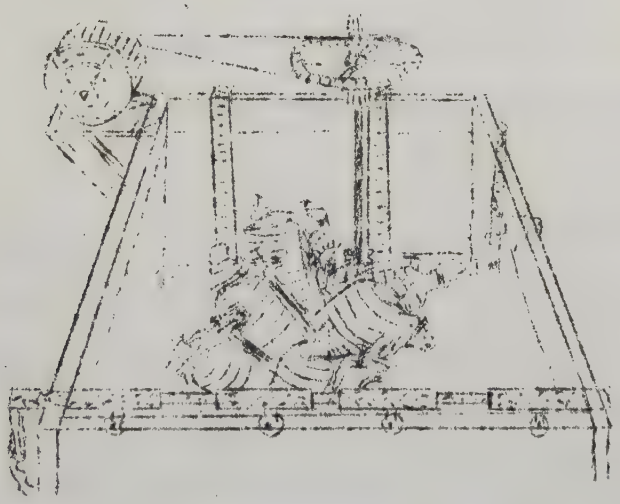


Figure 5
Bird's Eye View of Thermostat
Showing Motor, Driving Shaft, and Propeller Arrangement of Bottles in Bath.

In the construction of a thermostat of this kind it would be desirable to eliminate all steel work below the water line, as a good deal of trouble was caused by the rust making the water muddy. Furthermore, water lubrication had to be relied upon, and the worm gear and bearings wore out very rapidly. Bronze gears and wood block bearings were substituted in the later work, and were muck more satisfactory. It would be desirable to make the hanger cradle, shafts, gears, bolts and everything of bronze. The motor

The motor has given a great deal of trouble, due to wearing of the brushes, and the simpler less expensive split-phase motor which has no brushes would be more satisfactory. Such a motor has a low starting torque, but this is no disadvantage for this purpose, since the loads are always relatively small.

Each of the bronze frames on the long horizontal shaft carries four ordinary 2400 milliliter acid bottles, with the bottom of each resting in a triangular base next to the shaft, the necks passing thru bronze forks which can be screwed down to hold the bottles firmly in position. The bolts holding these forks and retaining nuts were set in holes in the frames which had been filled with molten solder, and were then secured

by a bronze brad driven thru a small hole drilled thru bolt and frame. This arrangement holds the bottles end to end firmly and safely.

The frames are staggered along the shaft so as to form a sort of screw propeller, to create a powerful stirring effect on the water in the the tank. By this arrangement as many as twenty bottles can be rotated at one time, altho it was found advisable to remove one frame to make room for a settling rack, leaving sixteen in motion and five in the rack. The gear ratio was designed to give the main shaft a speed of ten revolutions per minute; too great a speed would defeat the purpose by causing centrifugal action, which would keep the solid at one extreme end of the bottle and prevent intimate contact of the two phases.

The thermo-regulator was of the bimetallic type, made by the Thermo-Electric Instrument Company, of Newark, N. J. An accuracy of plus or minus 0.1 ^{o} C. was claimed for it, carrying 0.5 ampere current thru the contact points; but a fluctuation of at least one degree was found, and the contacts arced badly, fusing together so badly at times that they had to be pulled apart with the fingers, even when only 0.25 ampere was being used. A magnetic relay operated by a six volt Edison storage battery was then installed, so that only a very small current passed thru the thermo-regulator itself, the heavy heating current passing thru the carbon contact points of the

relay. This arrangement worked beautifully, giving a constancy of plus or minus 0.05° C. over long periods of time. The heating was effected by four 250-watt heater bulbs, but the whole bank was used only to bring the bath up to temperature after it had been refilled, one bulb being sufficient for ordinary regulation.

The accompanying drawings show clearly the whole construction, and it is believed that this thermostat, developed after a great amount of tedious experiment, is more suitable for purposes of this kind than any that has been yet described.

Acknowledgement is gratefully made to Mr. F. W. Fullerton, Mechanician of the School of Chemistry of the University of Minnesota, for its skillful construction, and for valuable suggestions during the period of development.

Bottles. The large bottles were tested for leakage, and stoppers ground in where necessary; then the tops of the stoppers were ground shorter, with a little groove so they could be wired on, and wire collars with loops placed permanently on the necks of the bottles. Both stoppers and bottles were then given etched numbers, and aged in distilled water for over a year to dissolve out soluble salts. This precaution was justified by the attaining of unweighable blanks in most cases, and by getting a specific conductance of 1.7×10^{-6} on a sample of conductivity water which had been kept in one for several weeks.

Time required for saturation. In order to determine the time required for complete saturation, a number of determinations were made on lanthanum oxalate in 4-normal hydrochloric acid, taking samples at nine, eighteen, and twenty-six hours. The results are shown on the curve in figure 6. Saturation was nearly, but not quite complete at the end of nine hours; and no further gain was registered between eighteen and twenty-six hours. Plenty of material was available for this test and a large excess of solid phase was used. Under such circumstances twenty-four hours are sufficient, but is the case of very rare materials where a large excess cannot be used it would probably take much longer to come to equilibrium. In general each bottle was kept turning over in the bath for at least a week, and many longer, so there was no doubt about complete saturation being attained. A much longer time has thus been allowed for saturation than has been done by any previous investigator, Hauser and Wirth agitating the solutions for twenty-four hours and all other investigators presumably being satisfied with a much shorter time of contact. While a day may possibly be sufficient it leaves no margin of safety; and to allow only twenty minutes, as was done for some conductivity determinations, is out of the question.

Experimental method. The materials were lightly ground in an agate mortar to break up any lumps, vigorous grinding being avoided to prevent the decomposition of the oxalates by heat.

To make a determination, some acid of known concentration was placed in one of the clean dry bottles and an excess of powdered oxalate added. The ground glass stopper was then wired on and paraffined, then rotated for a week, at the end of which time it was removed from the shaft and set in the settling rack for at least eight or ten hours. Some samples settled clear in an hour, but others, especially the low acid concentrations and water samples, settled very slowly.

The removal of suspended solid from the solutions presented quite a serious problem. At first, filtration was attempted, discarding the first portions passing thru, but this was found to be hopeless. The long grinding in the rotating bottles reduced the material to an extremely fine state of subdivision, and the filtrate thru even hardened paper was opalescent. Furthermore, filtration was slow and messy, and introduced disturbing factors like adsorption in the pores of the paper, evaporation, and temperature changes. Therefore filtration was definitely abandoned. Next, cautious pipetteing by slow mechanical suction was tried, and was fairly satisfactory but left much to be desired. Where more than one pipettefull was required, taking a sample was very troublesome, as the least amount of liquid flowing back into the bottle disturbed the solid, so that it had to be allowed to settle again.

By far the fastest, most convenient and accurate method of removing the solution from excess of solid was found to be by means of a simple pressure pipette (Fig. 7).

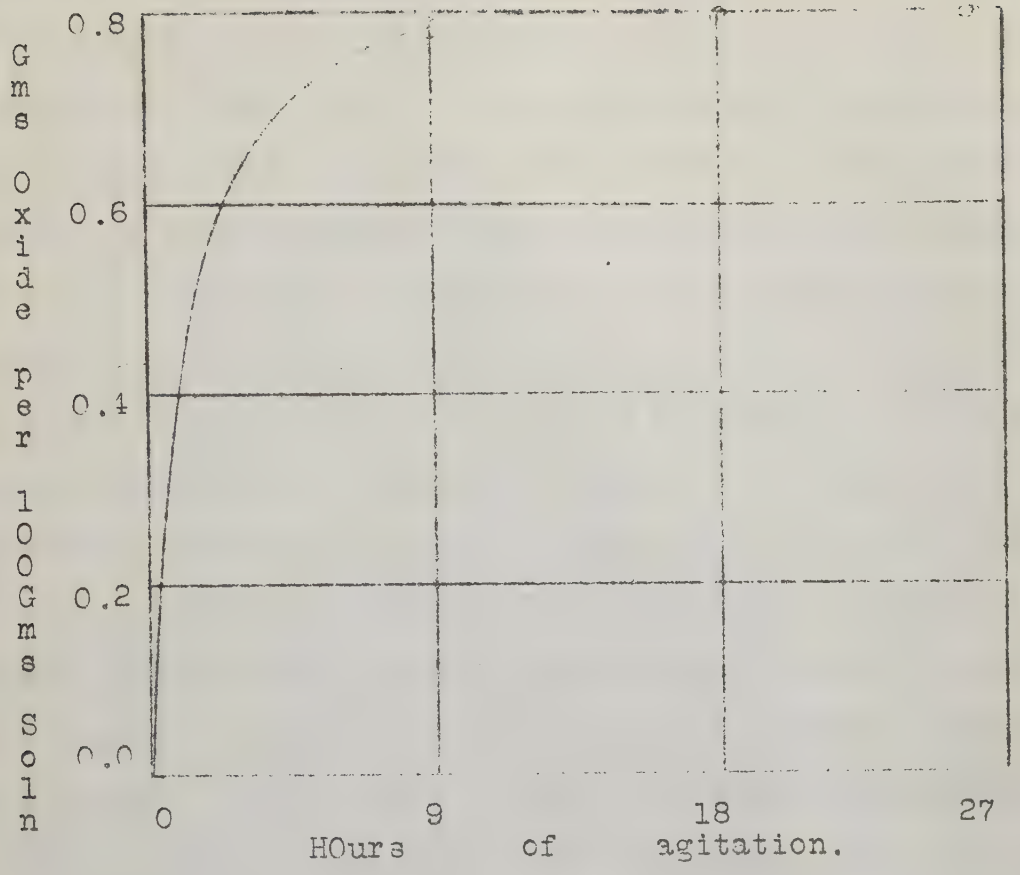
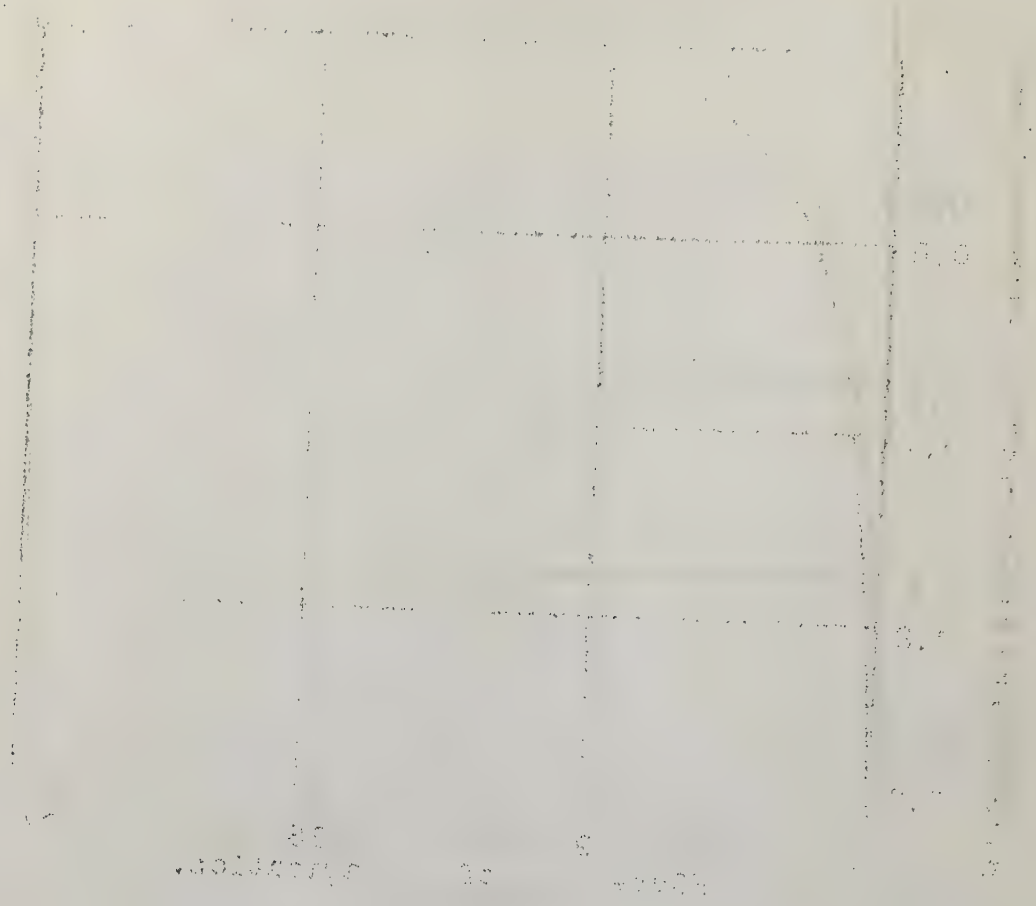
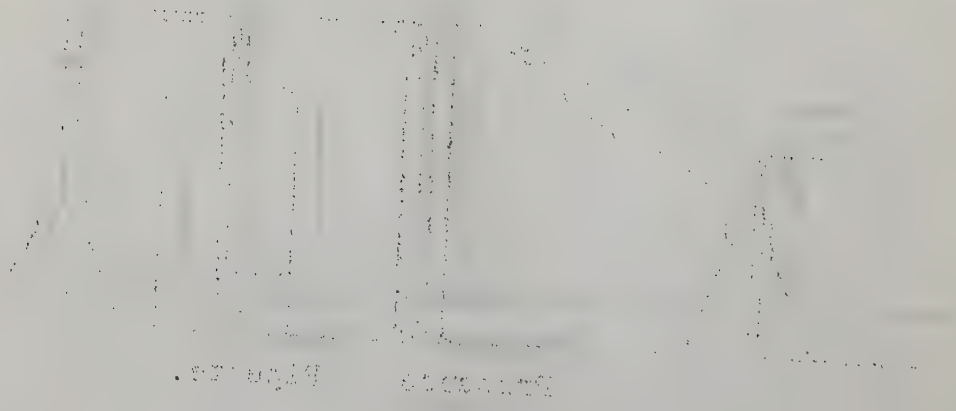


Figure 6

Pressure Pipette.

Figure 7





The glass tube was bent so as to lie flat on the bottom of the bottle, the mouth being spread to a fan shape and pointed slightly upward. This draws a wide flat stream of solution downward toward the solid rather than away from it, thus minimizing the danger of drawing some of the solid out with the sample. Furthermore it permits the taking of large samples, say one kilogram, at a single operation, only a fraction of the time being required compared with that needed for sucking up the sample in the usual way. The air was washed and dried to prevent any possible contamination, and a constant pressure overflow inserted between the wash bottles and pipette. With the stop-cock on the pipette colsed, pressure was turned on until excess air began to escape thru the pressure regulator; when the cock was opened, liquid began to flow, and when the desired amount had passed over, the cock was closed again. Thus the solid in the bottle was not disturbed, and the duplicate sample could be taken at once. When both samples had been taken, the pressure was released, the stop-cock opened, and all the liquid in the pipette siphoned back into the bottle, so there was no loss of materials. This is a very important consideration in work of this kind where materials are rare and valuable.

A few samples were purposely taken before the liquid had settled quite clear, and the results were much too high despite the fact that the opalescent solution was filtered thru the finest paper. This demonstrates the utter inadequacy of filtration for removal of suspended oxalates, at least after such

agitation as was received in these tests. So it seems that the method here described is the best for the purpose. Every sample was carefully examined for suspended solid and discarded if any was found.

Samples varying in amount from 50 grams to 1 kilogram according to the nature of the solvent, were weighed in Erlenmeyer flasks, and then transferred little by little to small weighed porcelain dishes of about 60 cc capacity. Evaporation to dryness was accomplished over distilled water in an electrically heated water bath, a reinforced plate glass cover being installed a few inches above the dishes to protect from dust. These dishes weighed only about 45 grams, - little more than a large platinum crucible, - so the sensitivity of the balance was not materially affected; and by evaporating large samples in small portions the difficulty in obtaining the correct weights of small amounts of material in large dishes was avoided. These dishes were always ignited against a tare dish of similar size which had been subjected to the same processes of heating and cooling, thus compensating for any variations of humidity, pressure, etc.

The samples were first gently ignited to change the oxalates to carbonates, and then treated with concentrated, redistilled nitric acid to expel chlorides in the case of the hydrochloric acid solubility tests, and to help oxidize carbon in all cases. After the addition of the nitric acid they were again evaporated to dryness, and ignited to constant weight. Blanks for

an equal amount of the water or acid solution used were determined and the weight thus found was deducted from each determination where appreciable.

In this connection it is well to discuss the weighing form for the various determinations. As just pointed out, it is necessary to expel the chloride ion from the hydrochloric acid determinations by treatment with nitric acid. The expulsion of sulphate by simple ignition had been commonly accepted as easy. By chance the first sulphuric acid solubility determined in this investigation was of praseodymium, where the change from sulphate to oxide would be accompanied by color change, from light green to dark brown; and neither Meker burner nor blast lamp occasioned the slightest color change. This directed attention to statements in the literature regarding decomposition of the sulphates, that it is only at white heat that a rare earth sulphate can be completely converted to oxide, and that except in the case of cerium they form basic sulphates stable at 1000°C.[14] Since these large porcelain dishes are difficult to heat to a very high temperature, one was tested by means of a thermo-couple, and about 700°C was obtained over a blast with the dish covered, and 600°-650°C with open dish. This is entirely inadequate for complete conversion of the sulphates to oxides, so it was decided to weigh as anhydrous sulphates. The anhydrous sulphates as a weighing form have been criticised in the case of atomic weight determinations, on account of the great hygroscopocity;

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14. Matignon, Compt. rend., 134, 657 (1902) (Nd, Pr); 141, 1230 (1905) (Sm); 142, 394 (1906); Wild, Z. anorg. Chem., 47, 464 (1905) (La, Sm, Y, Er, Yb); L. Wöhler and Grundzug, Ber., 46, 1726 (1913) (La, Pr, Nd, Sm, Gd, Y, Er, Yb, Lu).

but by making the weighings rapidly it was possible to obtain accurate results. The samples were heated for several hours in a muffle furnace at 500°C, the temperature being observed with a calibrated thermocouple. These ignitions were very tedious, but it is believed that the results were good. It is interesting to note that values of lanthanum oxalate in varying concentrations of sulfuric acid obtained by Hauser and Wirth[15] form a curve considerably higher than that obtained in this investigation by weighing as sulphates, and we feel justified in claiming that the results recorded by Hauser and Wirth, and by all other investigators who have based their figures on the conversion of sulphates to oxides by ignition are totally unreliable. On the assumption that it was the basic sulphate, $La_2O_3.SO_3$ and not La_2O_3 that Hauser and Wirth weighed, we have recalculated their results, and find that the revised values fall squarely on the sulphate curve found in this laboratory.

In all the determinations considerable difficulty was experienced in obtaining constant weight. All the oxides except CeO_2 exhibited a well defined tendency to descend to a minimum, and then to gradually register appreciable gains on subsequent ignitions. Some samples were ignited as long as fifty hours, and weighed twenty five or thirty times. The gain on each new ignition was small, usually one or two tenths of a milligram, and these might easily be overlooked. In fact, on reviewing

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15. Hauser and Wirth, Z. anal. Chem., 47. 389 (1908).

some work done several years ago it was seen that weights then accepted as constant really had shown slight gains on the last weighings. The weight of the oxide would go down on successive ignitions over the blast, and then rise again gradually when ignited over the Meker burner. The explanation which first suggests itself is the formation of higher oxides, and on this point the literature[16] is contradictory.

In order to test this point, a sample of gadolinium oxide weighing 0.3001 g. was placed in a small glazed porcelain boat, and heated at varying temperatures in oxygen, hydrogen, and air, both in a combustion furnace and in the open air burners for over fifty hours. As a blank an empty boat was always run along under exactly the same conditions. The results of this run are given in the following table:

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16. Marc, Ber., 35 2370 (1902); Hermann, J. prakt. Chem., 82, 385 (1861); Zschiesche, Ibid., 107, 65 (1869); Jones, Am. Chem. J., 20, 345 (1898); Meyer and Koss, Ber., 35, 3740 (1902); Meyer, Z. anorg. Chem., 41, 119 (1904); Waegner, Z. anorg. Chem., 42, 118 (1904); Joye and Garnier, Compt. rend., 154, 510 (1912); Joye, Arch. Sci. phys. nat., IV, 36, 41 (1913); Brauner, Proc. Chem. Soc., 14, 72 (1898); 17, 56 (1901); Z. anorg. Chem. 32, 1 (1902); Cleve, Chem. News, 53, 30 (1886); Compt. rend., 97, 94 (1883); Bull. soc. chim., II, 43, 162 (1885); Trans. Chem. Soc., 43, 362 (1883); Benedicks, Z. anorg. Chem., 22, 393 (1900); Brinton and Pagel, J. Am. Chem. Soc., 45, 1460 (1923).

are given in the following table:

| | | |

Time	Temperature	Sourse of Heat	Medium	Weight
2 hrs.	700°C.	Elec. Comb. Fur.	H_2	4.2074 g.
2 "	"	"	"	4.2064
2 "	"	"	"	4.2060
3 "	"	"	"	4.2055
4 "	"	"	"	4.2054
3 "	1000	"	O_2	4.2053
6 "	700	"	"	4.2053
1 "	900	Meker Burner	Air	4.2054
2 "	"	" "	"	4.2056
3 "	"	" "	"	4.2059
4 "	"	" "	"	4.2063
7 "	700	Elec. Comb. Fur.	Dry Air	4.2065
2 "	"	" " "	" "	4.2067
5 "	"	" " "	" "	4.2066
5 "	"	" " "	" "	4.2066
4 "	"	Meker Burner	" "	4.2069

This shows that there is at first a loss in weight on ignition in hydrogen, but this is not regained on heating in oxygen. The sample had been obtained by ignition of the nitrate, and the loss may have been due to the decomposition having been incomplete at the start, although it does seem that a much shorter time should suffice for the breaking down of the nitrate. At any rate the evidence does not indicate the existence of a higher oxide. When heated in air over a Meker burner the sample immediately began to take on weight. When heated in an electric

furnace in dry, CO_2-free air. after a small initial gain, no further change was observed. Finally when heated in the open air again, another gain was registered.

It was thought that the sulphur from the illuminating gas might form stable sulphates, and the samples were accordingly tested for sulphates. Traces were indeed found, but hardly enough to account such large gains in weight. Fresh sticks of potassium hydroxide were kept in the desiccators, and this, together with the exercise of the greatest possible rapidity in weighing seems to preclude the absorption if carbon dioxide as a factor in the gains. The behavior is as yet unexplained, and in this investigation the minimum weight has been accepted as the constant weight. The sesquioxides were used as the basis of calculations, except in the case of cerium where CeO_2 was used, and for praseodymium the formula Pr_6O_{11} was adopted. Evidence for this formula in preference to the formerly accepted Pr_4O_7 has been clearly established[17]. In the determinations of the solubilities in sulphuric acid solutions the various elements were weighed in the form of anhydrous sesquisulphates, $R_2(SO_4)3$. In the case of cerium, however, owing to the comparative instability of cerous sulphate, and the ease with which ceric sulphate can be converted to ceria, the weighing form CeO_2 was used in all cerium determinations.

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17. Brinton and Pagel, J. Am. Chem. Soc., 45, 1460 (1923).

For the conductivity measurements the precision instruments described in Catalogue No. 48, of Leeds and Northrup, were used. This outfit included the Vreeland Oscillator, Curtis Coil Resistance Box, Kohlrausch drum-wound slide wire bridge, with extension coils, variable air condensers, cell, and Western Electric 2200 ohm radio telephones.

In the determination of the solubilities of some rare earth oxalates by the electrical conductivity method Rimbach and Schubert[18] placed some of the solid in conductivity water in the cell, and made measurements for twenty minutes, shaking the solution before each reading; and they found no increase in the conductivity at the end of this time. It is true that the change becomes quite slow at the end of twenty minutes, but the resistances of the solutions are so large, and the sound minimums correspondingly indistinct, that such a gradual increase in conductivity cannot be easily observed. To test this point some measurements were made in the same way, and at the end of an hour and a half the conductivity was still increasing, very slowly to be sure, but still decidedly more rapidly than could be accounted for by the simple absorption of atmospheric impurities by the solution.

For the determinations in this investigation the oxalates wereplaced in bottles with conductivity water, sealed, and turned over in the bath for several weeks, along with a bottle of pure water as a blank. At the end of this time the water gave a zero gravimetric blank from a liter sample, and a specific con-

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18 Loc. cit.

ductivity at 25°C of 1.67×10^{-6}. Gravimetric and conductivity determinations were then made, using one liter portions for the former. From Table I it is seen that satisfactory concordance of results was obtained by the two methods, and that our values are considerably higher than those reported by previous investigators, who used a technique in the conductivity determinations which while justified for ordinary work with salts of low valence, can scarcely be approved for the trivalent rare earth salts.

The values for the solubilities in acids of various concentrations at 25°C are shown in Table II.

The values have been plotted in a number of curves. The values of each table are first plotted on separate sets of curves to permit comparison of the different elements with each other under similar conditions. Then the mineral acid-oxalic acid combinations are plotted on different sheets for each element to show the effect of different conditions on each element. In this way a general view of the subject is obtained.

DISCUSSION

From an examination of the curves in Figs. 8, 9, and 10 it will be seen that the rare earth oxalates are most soluble in nitric acid, with hydrochloric and sulphuric acids following in order. These curves show no abnormality save that the La and the Ce curves cross, and the serial order is that of increasing atomic weights. The only previous work which has been done

are the solubilities in sulfuric acid by Hauser and Wirth referred to earlier in this paper. Their values for cerium agree in the main with values found in the present investigation, altho their values do not lie on a smooth curve. Their values for lanthanum and gadolinium would agree with those just found on the assumption that their supposed oxides were in reality basic sulphates. And the values for neodymium, and samarium agree fairly well, because these elements are less strongly basic and can more easily be converted to oxides.

They did not determine the solubilities of praseodymium exalate in sulfuric acid concentrations, which probably accounts for their failure to observe the incomplete change from sulfate to oxide, since it is only in the case of praseodymium that it is evident from a color change. The color change in the case of neodymium is not so marked, but is easily noticed once attention is called to it, and it takes long intense ignition to effect the change from pink to blue. Furthermore, a sample which had apparently changed over completely gave a considerable sulfate test. It has been our experience that lanthanum and praseodymium sulfates change over with the greatest difficulty, gadolinium coming next, with neodymium, samarium, and cerium following in order. This is only a qualitative observation, and there is some question as to the relative positions of neodymium and gadolinium, Gadolinium presents a number of abnormalities in its chemical and physical properties,[19] and this checks in a qualitative

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19. Brinton and James, J. Am. Chem. Soc., 43., 1446 (1921).

way the observation of Wöhler and Gründzweig[20] that the sulfate of gadolinium dissociates less easily than that of samarium. When samples are ignited in large porcelain dishes presenting a large radiating surface, it seems impossible to completely convert the sulfates of lanthanum, prasecdymium, and gadolinium to oxides, very difficult to convert that of neodymium, comparatively easy to convert that of samarium, and easy to convert the sulfate of cerium to oxide.

The addition of a small amount of excess oxalic acid to nitric acid reduces the solubilities in low concentrations of the latter considerably, but they are still quite large so that it would seem that a nitric acid solution is not suitable for a quantitative precipitation of the oxalates; this will be discussed more in detail under the individual elements. The curves in Figs. 11 and 12 exhibit no abnormalities as a whole, save that the the lanthanum curve tends to cross the others as usual.

From an examination of the curves in Figs. 15, 16, and 17, it will be seen that the solubility depression in the hydrochloric acid-oxalic acid mixtures is very much greater than in the nitric acid-oxalic acid mixtures. For example the solubility of lanthanum oxalate in double normal nitric acid saturated with oxalic acid is about eighteen per cent of that in pure double normal nitric acid; while the solubility in double normal hydrochloric acid saturated with oxalic acid is only about five

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20. Wöhler and Gründzweig, Ber., 46, 1726 (1913).

and one half per cent of that in pure double normal hydrochloric acid. In general the flat part of the curves is very much longer in the hydrochloric acid mixtures than in the nitric acid mixtures, so that the mineral acid concentration would not have to be controlled nearly si carefully for the former in order to secure quantitative precipitation. Many quantitative directions in the literature caution against the use of excessive amounts of oxalic acid while others recommend it. Hauser and Wirth in their very meritorious work found a trace of complex formation in sulfuric acid-oxalic acid mistures, which while not great caused them to recommend the use of only a moderate amount of oxalic acid. So for hydrochloric and nitric acids, it seems best to use about half normal oxalic acid with low concentrations of mineral acids, preferably hydrochloric.

Another thing of interest in these curves is the fact that gadolinium falls between neodymium and samarium, while solubility considerations in general place it between europium and terbium in the serial order,[21] and the hydrolysis of the sulfates and carbonates[22] accord it the same position. On the other hand, the dissociations of the anhydrous sulfates[23] and fractional precipitation with ammonium hydroxide[24] place it between neodymium and samarium. From the curves in Figs. 15, 16, and 17 it will be seen that the solubility evidence is not completely in accord with the serial order of increasing atomic weights.

SUMMARY

The solubilities of the elements of the Cerium Group of rare earths, lanthanum, cerium, prasecdymium, neodymium, and samarium, and of one element of the intermediate Terbium Group, namely gadolinium, in water, in hydrochloric, sulfuric, and nitric acids, and in mixtures of hydrochloric and nitric acids with oxalic acid have been measured.

Analytical conditions for the quantitative estimation of these elements have been determined, and their limitations discussed.

Apparatus and procedure for the rapid and accurate determination of solubilities has been developed for future work.

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21. Katz and James, J. Am. Chem. Soc., 36, 779 (1914).
22. Brinton and James, Loc. cit.
23. Wöhler and Gründzweig, Loc. cit.
24. de Bois baudran, Comnt. rend., 111, 393 (1890); Benedicks, Z. anorg. Chem., 22, 398 (1900).

TABLE I

Water Solubilities in Milligrams per Liter at 25° C.

	La	Ce	Pr	Nd	Sm	
Gravimetric Determination	2.14	1.09	1.49	1.48	1.46	mg.Ox/l.
Conductivity "	2.04	0.80	2.12	1.95	1.47	" " /l.
" "						
Rimbach & Schubert	0.62	0.41	0.74	0.49	0.54	" " /l.

TABLE II.

Solubilities in Acids in Gms. Oxides per 100 Gms. Solution at 25° C.

NORMALITY Mineral Acid	NORMALITY Oxalic Acid	RARE EARTH OXIDE La	Ce	Pr	Nd	Sm	Gd
HCl							
0.1008	------	0.0129	0.0083	0.0061	0.0046	0.0037	0.0015
0.2576	-------	0.0341	0.0238	0.0174	0.0132	0.0112	0.0062
0.5004	------	0.0833	0.0533	0.0400	0.0269	0.0266	0.0206
1.0180	------	0.2330	0.1376	0.1020	0.0768	0.0675	0.0588
2.0000	------	0.4072	0.3491	0.2563	0.2041	0.1427	0.1540
5.2000	------	0.7730	------	------	0.9344	------	------
2.0000	0.1	0.1303	0.1342	0.0726	0.0455	0.0261	0.0329
4.0000	0.1	0.6170	0.7290	0.4330	0.3393	0.1973	0.2368
2.0000	0.5	0.0389	0.0218	0.0108	0.0068	0.0038	0.0023
4.0000	0.5	0.1880	0.2410	0.1143	0.0638	0.0367	0.0424
6.0000	Sat'd.	0.3351	0.1981	0.0932	0.1105	0.0720	0,1204
4.0000	Sat'd.	0.1072	0.1178	0.0615	0.0472	0.0176	0.0298
HNO_3							
0.2482	------	0.0223	0.0225	0.0180	0.0146	0.0117	0.0137
1.9920	------	0.5796	0.4324	0.3200	0.2611	0.2132	0.1750
4.0740	------	1.6170	1.4340	1.0325	0.8251	0.6578	0.5662
2.0000	0.1	0.2751	0.2001	0.0808	0.0694	0.0559	0.0485
4.0000	0.1	0.9140	1.1000	0.6600	------	0.3910	0.3447
2.0000	0.5	0.0777	0.0333	0.0192	0.0119	0.0083	0.0080
4.0000	0.5	0.4330	0.5021	0.2487	0.1540	0.0995	0.0876
4.0000	Sat'd.	0.1610	0.2541	0.0414	0.0592	------	0.0240
6.0000	Sat'd.	0.7350	0.8520	0.5696	0.2080	------	0,0769
H_2SO_4							
0.0860	------	0.0175	0.0090	0.0066	0.0053	0.0056	0.0056
0.4190	------	0.0682	0.0472	0.0321	0.0254	0.0264	0.0255
0.9580	------	0.1547	0.1100	0.0809	0.0642	0.0644	0.0614
1.8160	------	0.3102	0.2417	0.1753	0.1363	0.1366	0.1285
2.6120	------	0.4120	0.3737	0.2628	0.1497	------	0.1362

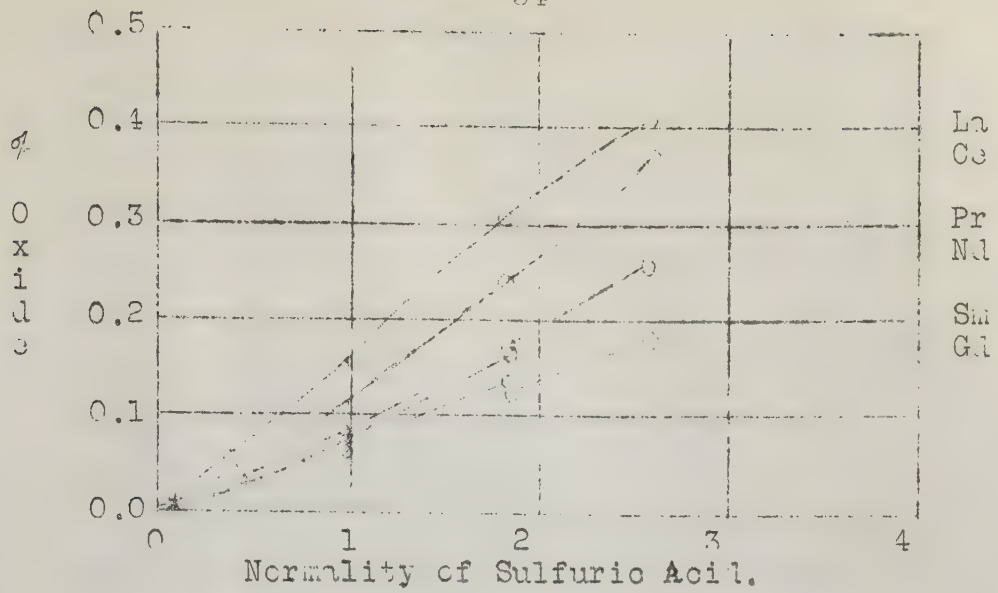


Figure 8

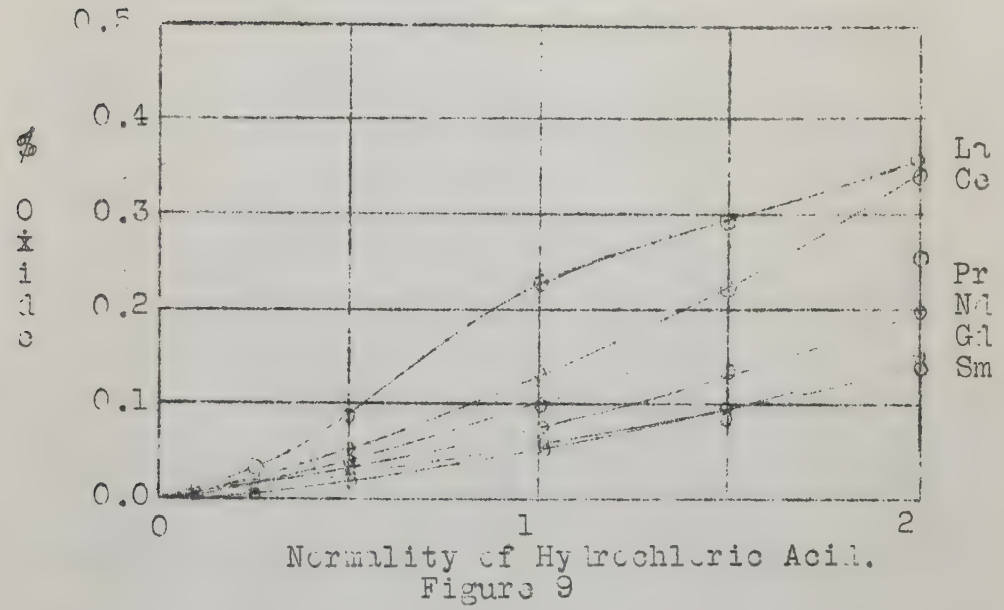


Figure 9

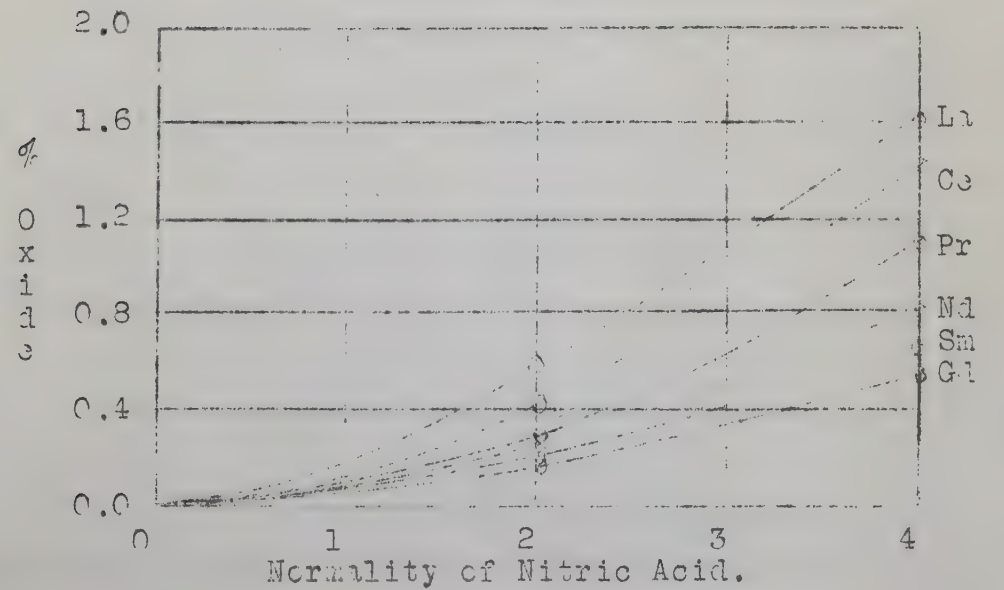
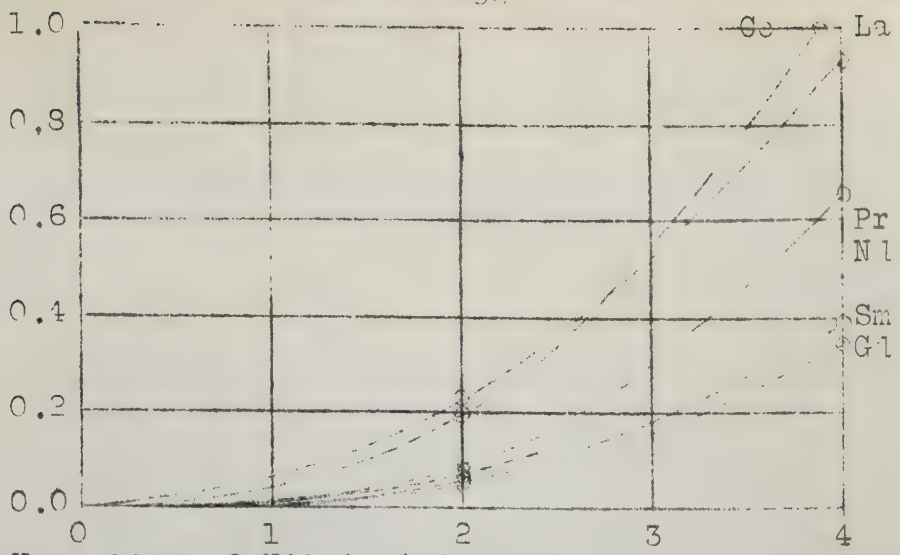
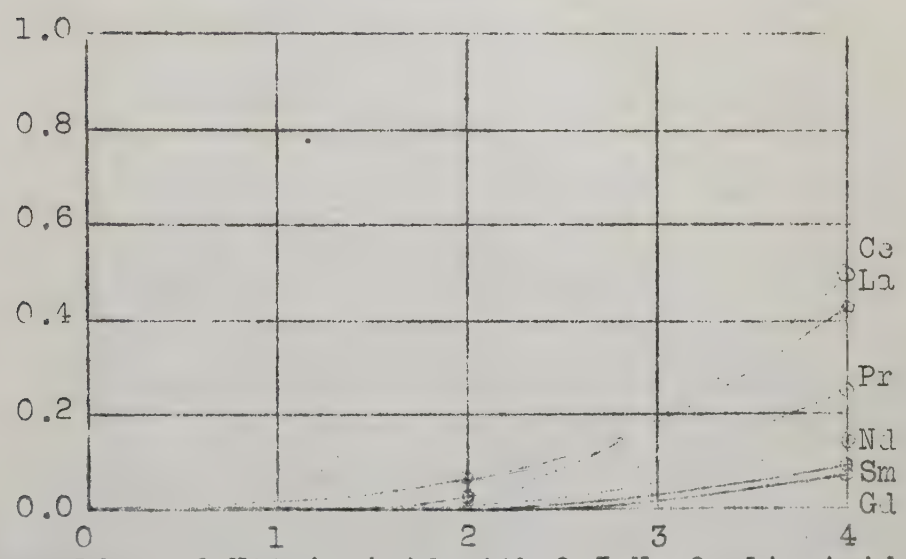


Figure 10



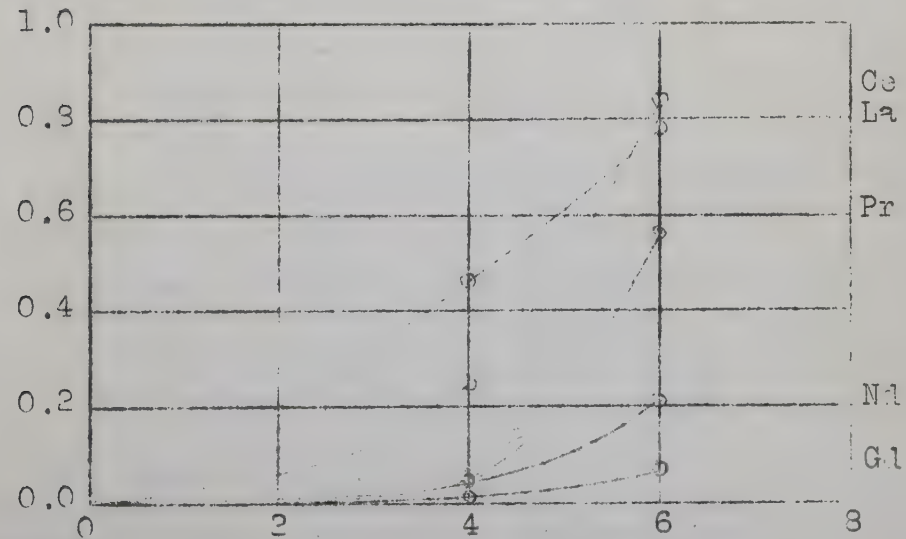
Normality of Nitric Acid with 0.1 N. Oxalic Acid.

Figure 11



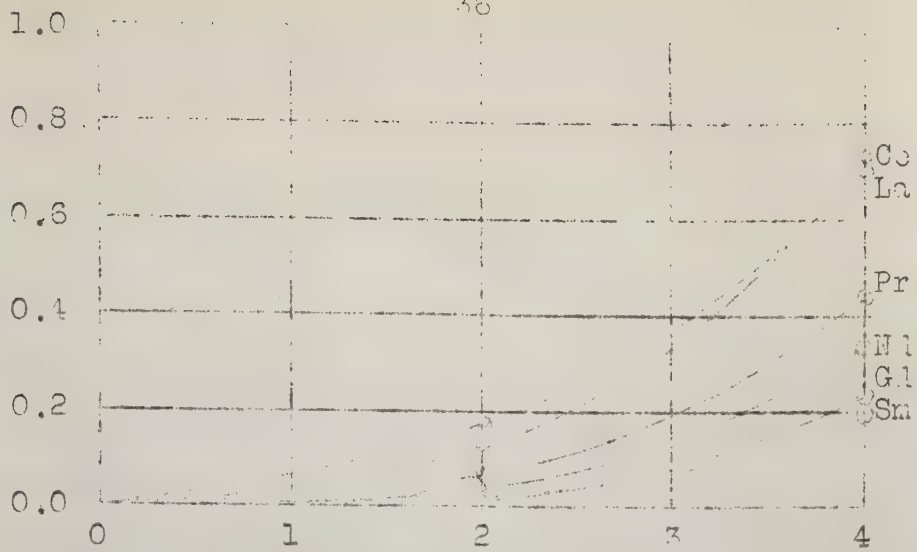
Normality of Nitric Acid with 0.5 N. Oxalic Acid.

Figure 12



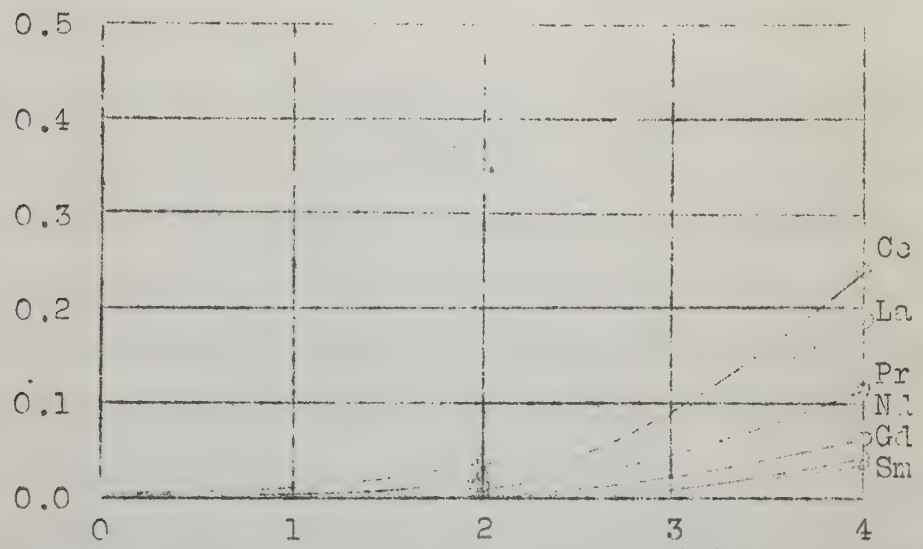
Normality of Nitric Acid Saturated with Oxalic Acid.

Figure 13



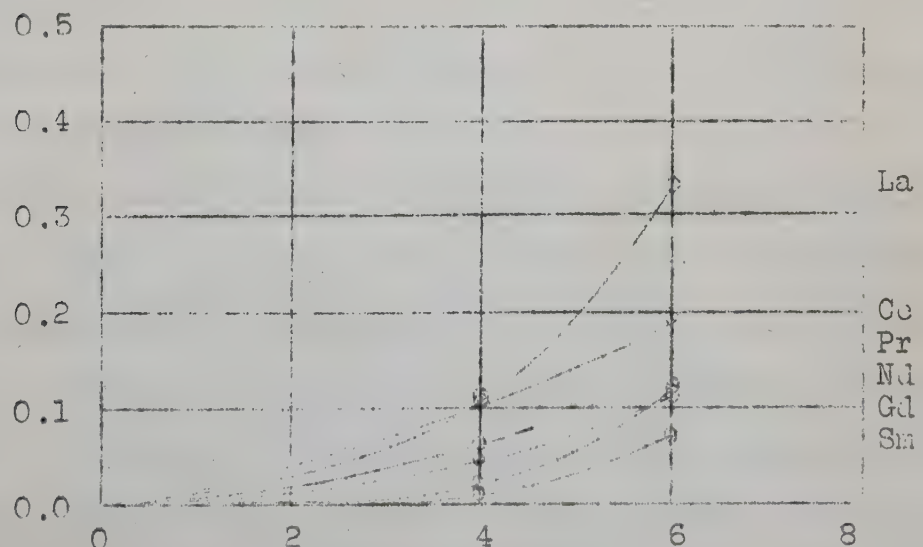
Normality of Hydrochloric Acid with 0.1 N. Oxalic Acid.

Figure 14



Normality of Hydrochloric Acid with 0.5 N. Oxalic Acid.

Figure 15



Normality of Hydrochloric Acid Saturated with Oxalic Acid.

Figure 16

VITA

The author was born at Petersburg, West Virginia, on January 26, 1896. After several years in private schools he entered McDonough Institute, LaPlata, Maryland, in 1908, where he remained until 1911. The year 1911-12 was spent at Randolph-Macon Academy, Front Royal, Virginia, and in the fall of 1912 he entered Randolph-Macon College, Ashland, Virginia, with advanced standing. He received the degree of Bachelor of Arts therefrom in 1915.

He was Instructor in Mathematics in Randolph-Macon College for the year 1914-15; and for the following year he was Instructor in Chemistry and Mathematics in the Fredericksburg, Virginia, High School. In the fall of 1916 he received an appointment as Assistant in Chemistry in Yale University, and entered the Graduate School there. In 1917 he was appointed Scholar from West Virginia and Assistant in Chemistry at Johns Hopkins University, but enlisted in the army in November.

After several months service as chemical assistant to the division gas officer at Camp Lee, Virginia, he was transferred to the research division of the gas service, from which he was discharged in January, 1919.

He was at once appointed Instructor in Chemistry at Lafayette College, Easton, Pennsylvania. After completing a piece of research under the direction of Dr. E. C. Bingham on the "Fluidities and Specific Volumes of Benzene and Benzyl Benzoate" he received the degree of Master of Science from Lafayette College in June, 1919. The results of this research were published

in the Journal of the American Chemical Society in October, 1920.

A lung collapse attributed to delayed effects of gas poisoning caused an enforced idleness for over a year, and in the fall of 1920 he was appointed Instructor in Chemistry in the University of Minnesota. In October, 1923, he published in conjunction with P. H. M.-P. Brinton and Arthur E. Stoppel an article on "The Titration of Hydrofluoric and Hydrofluosilicic Acids in Mixtures containing Small Amounts of Hydrofluosilicic Acid."

The following year he completed the requirements for the degree of Doctor of Philosophy, Major, the Analytical Chemistry of the Rare Elements, Minor, Physical Chemistry, at the University of Minnesota, and the degree was conferred in July, 1924.